Electro-oxidation behavior of tungsten carbide electrode in different electrolytes ①

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Abstract: The electrochemical activity and stability of tungsten carbide gas diffusion electrode in different electrolytes were determined by galvanostatic charge method. It is shown that WC exhibits good electrocatalytic activity and stability for hydrogen oxidation in acidic solutions when the electrode potential is below about 800 mV(vs DHE), WC is firstly oxidized to an unstable blue tungsten oxides at 800 - 900 mV which are closed to a composite stoichiometry of W_2O_5 in H_2SO_4 solution and W_8O_{23} in HCl solution calculated by charge consumed . Furthermore, the generated intermediate tungsten oxides can be further oxidized into WO_3 at higher potentials. While in alkali solution, WC can not be used as anodic catalyst for its poor stability and catalytic activity due to the fact that WC will be directly oxidized into WO_3.

Key words: tungsten carbide; electrocatalyst; electrochemical behavior

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1 INTRODUCTION

Fuel cells are receiving increased recognition as a notable alternative to our present power sources because they exhibit high operational efficiencies and impressive environmental acceptability. Unfortunately, efficient electrocatalysts for electrochemical reactions of the fuel are still far from satisfactory. In order to increase the oxidation rate and improve electrode stability, considerable efforts have been mainly directed towards the study of Pt and Pt-based bimetallic (or multimetallic) alloys, such as Pt/ Ru, Pt/ Rh, Pt/ Sn, Pt/ Ru/ Mo, Pt/ Ru/ WO_x. However, platinum is expensive and readily poisoned by carbon monoxide (CO) existing in the fuel. So recently, great interest has been transferred to develop new non-noble metal electrocatalysts.

Since the discovery of the catalytic activity of tungsten carbide for hydrogen ionization in acid solutions by Böhm et al[1] in 1968, numerous studies have been conducted on the uses of tungsten carbide in catalysis. Boudart et al[2] reported that tungsten carbide(WC) displayed "platinum-like" behavior in surface catalysis. Subsequently, tungsten carbide was also founded to compare favorably with platinum as an electrode for hydrogen oxidation and excellent resistance to poisoning[3-11]. Our previous works have further shown that the electrocatalysts with major phase of tungsten carbide exhibit high electrocatalytic activity for hydrogen anodic oxidation in HCl solutions[12-15]. However, even after more than thirty years of fundamental studies, the oxidation and stability of tungsten carbide itself used as electrode material is still not well understood until now. The aim of the present work is to investigate the electrochemical stability of tungsten carbide gas diffusion electrode in different electrolyte solutions by the use of galvanostatic charge method.

2 EXPERIMENTAL

The preparation and characterization of the tungsten carbide electrocatalysts with specific surface area 25 - 30 m^2/ g were described in our previous work[12, 13]. The gas diffusion electrode was mainly composed of two water-proof conductive permeable films and metal mesh substrate sandwiched by cold pressing at 50 MPa for 5 min, and then sintered in N_2 atmosphere at 350 ℃ for 30 min. Tungsten carbide powders were embedded into one side of the sintered electrode, which used as catalytic membrane. The geometric surface area of each electrode was about 6.5 cm^2 with the loading of 6.15 mg/ cm^2. The preparation methods of the water-proof conductive permeable film was the same as those described in the literature[14].

Electrochemical measurements were performed using an EG&G PARC Model 273A potentiostat controlled by M 270 electrochemical analysis software and a three-electrode electrochemical cell. The data were acquired with a personal computer automatically. The counter electrode was a platinum plate. Dynamic hydrogen electrode (DHE) was used as the reference electrode. All the potentials are reported with respect to the DHE. The electrolytes were made from analytical grade reagents and distilled water. The test temperature was controlled at 40 ±0.5 ℃ and gas flow rate was held constant at about 30 cm^3/min.

To evaluate the adsorptive ability of hydrogen on tungsten carbide, a series of anodic charge measurements were conducted under different atmospheres in 3.5 mol/L HCl solution as described follows: 1) high purity H_2 was first fed into the gas chamber for one hour, and then introduced N_2; 2) high purity N_2 was fed into the gas chamber throughout the whole process. The galvanostatic charge current was all maintained at 10 mA.

To investigate the electrochemical stability of tungsten carbide electrode in different electrolytes, the electrode was firstly kept in a flow of hydrogen for 20 min to eliminate trapped air inside the pores, and then immersed into the electrochemical cell. In every case, an anodic current of 20 mA was applied to measure the hydrogen anodic ionization curves under H_2 ambient. Subsequently, to replace H_2 with N_2, electrochemical oxidation behavior of tungsten carbide was carried out under the same electrolytic conditions. The structural transformations of tungsten carbide during the oxidation were characterized by X-ray diffraction (XRD) and sorption analysis.

3 RESULTS AND DISCUSSION

As reported previously, the electro-catalytic activity of tungsten carbide was dependent highly upon the chemical status of the surface. Therefore, to some extent, it can be evaluated by measuring the amount of adsorbed reactants on the tungsten carbide. Fig. 1 shows the anodic charge curves of tungsten carbide electrode in 3.5 mol/L HCl solution and it is apparent that an obvious plateau exists for each curve. By comparing curves A with B, it is found that the potential rises slower in the presence of H_2 at the beginning of anodic charge process(labeled as line ab). According to Ref.[15], this can be ascribed to the oxidation of hydrogen absorbed on the surface of tungsten carbide. The overall reaction can be expressed as
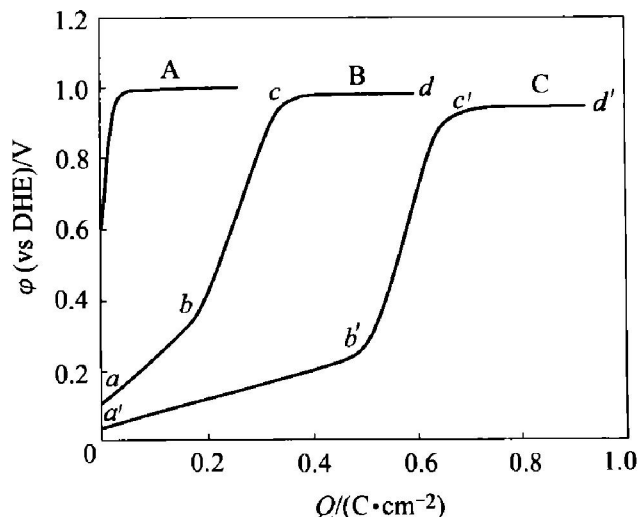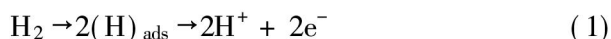
$$H_2 \rightarrow 2(H)_{ads} \rightarrow 2H^+ + 2e^- \qquad (1)$$

ig. 1   Anodic charge curves of tungsten carbide
n 3.5 mol/L HCl solution , applied 10 mA current
(A —WC electrode under flowing N_2;
B —WC electrode under flowing H_2 followed by N_2;
C —Pt electrode originated from Ref.[15])

On the other hand, the charge consumed by hydrogen adsorption and ionization on WC and Pt electrode was 0.17 C/cm^2 and 0.48 C/cm^2, respectively, which proved that the tungsten carbide exhibited lower electrocatalytic activity for hydrogen oxidation in HCl solution than platinum. Nevertheless, compared with the other electrocatalysts such as metal carbides, borides and silicides as reported previously[10], the as-prepared WC had higher adsorptive ability of hydrogen and electrocatalytic activity for hydrogen oxidation in acidic solution. When H_2 was replaced by N_2 during the charge process, it was seen that the shapes of curves B and C were similar to curve A. The introduced charge was mainly consumed by charge of double layer and oxidation of electrode itself. The latter process can be described as follows:

$$(H_2O)_{ads} \longrightarrow (OH)_{ads} + H^+ + e^- \qquad (2)$$

$$(OH)_{ads} \longrightarrow O_{ads} + H^+ + e^- \qquad (3)$$
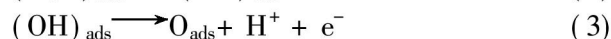
Subsequently, the adsorbed oxygen O_{ads} would react with tungsten carbide to form a layer of oxides on the electrode surface and its electrochemical stability would be debased accordingly.

Furthermore, the anodic charge performances of WC electrode were carried out in 2.0 mol/L H_2SO_4 and 3.5 mol/L HCl electrolyte, respectively. As shown in Fig. 2, the electrochemical behavior of WC electrode in the above electrolyte solutions is very similar. For example, the potential of hydrogen oxidation was about 420 mV on the observation of plateau 1, and this plateau would be prolonged if H_2 was introduced continuously into the gas chamber (seen dot lines in the figure). Once H_2 is substituted by N_2, the charge potential increased quickly to about 800 mV, plateaus 2 and 3 appeared as a consequence of the oxidation of tungsten carbide. Simultaneously,
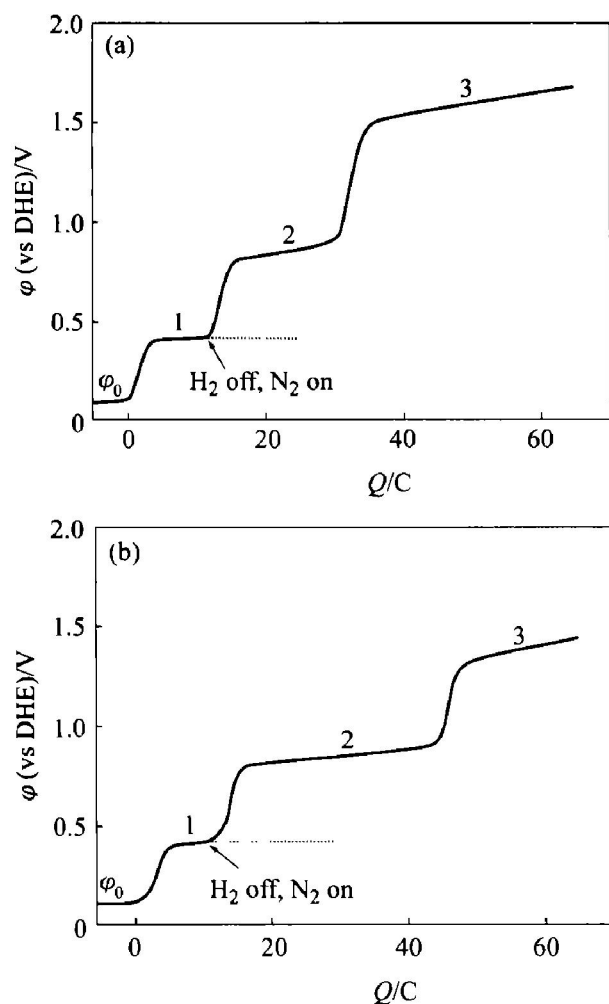
Fig. 2 Anodic charge curves of WC electrode in different acidic solutions, applied 20 mA current
(a) —2. 0 mol/ L H_2SO_4 solution;
(b) —3. 50 mol/ L HCl solution

Fig. 3 Anodic charge curve of WC electrode in 2. 5 mol/ L KOH solution
(Applied current 20 mA)

In addition to the oxidation of WC, the O_2 in H_2SO_4 solution and Cl_2 evolution in HCl solution were also observed when the anodic charge was continued. The detailed results are summarized in Table 1.

In this paper, the anodic properties of WC electrode in alkali solution was also investigated. Fig. 3 depicts the anodic charge behavior of WC electrode in 2. 5 mol/ L KOH solution. As shown in Fig. 3, the polarization of hydrogen oxidation on WC electrode is more severe than in the case of acidic solutions. The potential of plateau 1 is about 830 mV, which is identical to that of plateau 2 in acidic solutions. This implies that the major reaction is the electro-oxidation of WC electrode rather than the oxidation of hydrogen. When H_2 is substituted by N_2, the electrode potential has a slight increase(as shown in plateau 2) and the color of electrode surface turns into yellow gradually, which is WO_3 characterized by XRD analysis. Consequently, the as-prepared WC is not a stable and suitable electrocatalyst for the hydrogen oxidation in alkali solution. When WC is oxidized completely, the introduced charge is continuously consumed by oxygen evolving reaction occurring in the potential of plateau 3. The detailed results of WC electrode in KOH solution are also listed in Table 1.

the color of electrode would change into blue and yellow in succession. The major phase of blue substances formed on the electrode surface were W_2O_5 and W_8O_{23} in H_2SO_4 and HCl solutions, respectively, and both of the yellow substances were WO_3 calculated by charge consumed. According to the above results, the number of electrons transferred during the first step of WC oxidation were 1 in H_2SO_4 and 1. 75 in HCl solution, respectively. The overall electrochemical reaction of WC in acidic solutions can be written as
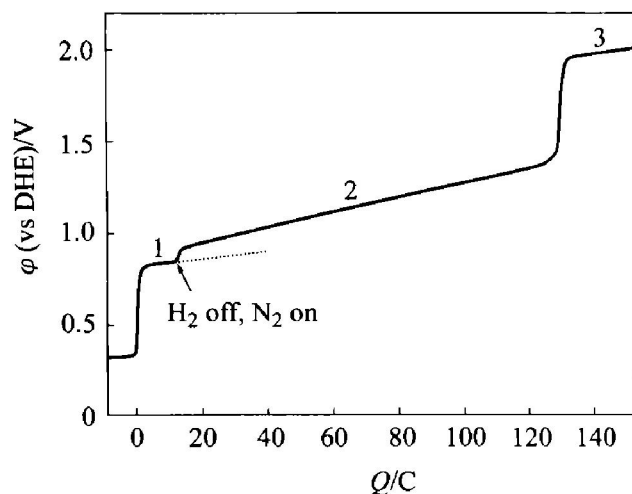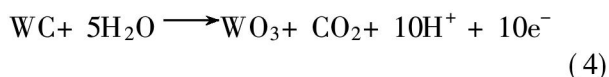
$$WC + 5H_2O \longrightarrow WO_3 + CO_2 + 10H^+ + 10e^- \quad (4)$$

Table 1 Detailed electrode processes of WC anode in different electrolyte solutions

Electrolyte solution	Open circuit potential / mV	Plateau 1		Plateau 2			Plateau 3		
		Potential/ mV	Electrode process	Potential/ mV	Charge Consumed/ C	Products	Potential/ mV	Product	Other reaction
2. 0 mol/ L H_2SO_4	~ 80	~ 420	H_2 oxidation	800 ~ 900	19. 6	W_2O_5+ C	> 1 500	WO_3	O_2 evolution
3. 5 mol/ L HCl	~ 80	~ 420	H_2 oxidation	800 ~ 900	34. 7	W_8O_{23}+ C	> 1 300	WO_3	Cl_2 evolution
2. 5 mol/ L KOH	~ 350	830 ~ 850	H_2 oxidation and partial oxidation of WC	900 ~ 1300	115	WO_3+ CO_2	> 1 900	WO_3	O_2 evolution

4 CONCLUSIONS

The WC electrode exhibits high electrochemical stability for hydrogen ionization in acidic electrolytes when the potential is below 800 mV. So, it is suitable to be used as the anodic electrocatalyst for hydrogen ionization in H_2-O_2 or H_2-Cl_2 fuel cell. In alkali solution, the electrocatalytic activity and stability of WC for hydrogen oxidation are low and can not be used as an anodic electrocatalyst due to the fact that WC would be directly oxidized into WO_3.

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